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폐 글리세롤과 돈분의 혼합 소화

김상현†, Shihwu Sung*
대구대학교 환경공학과
미국 아이오와주립대학교 토목건설환경공학과*
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Co-digestion of Waste Glycerol with Swine Manure

Sang-Hyoun Kim†, Shihwu Sung*
Department of Environmental Engineering, Daegu University
Department of Civil, Construction, and Environmental Engineering, Iowa State University, USA*

ABSTRACT

Production of crude glycerol from biodiesel industry is expected to exceed the commercial demand for purified glycerol in the near future. This study aimed to evaluate the feasibility of co-digestion of crude glycerol with swine manure. Crude glycerol up to 13.8 g/L was regarded as a good co-substrate for swine manure digester. It improved methane production and productivity by 90% and 120%, respectively. Methane yield of crude glycerol at the condition was estimated to be 232 mL/g. However, it inhibited methanogenic activity at above 27.5 g/L. Optimum concentration of crude glycerol for co-digestion with swine manure would be near to 13.8 g/L.

Keywords : co-digestion, glycerol, inhibition, swine manure

†Corresponding author : sanghkim1@daegu.ac.kr

초 록

바이오디젤 과정에서 부산물로 발생하는 글리세롤의 양은 가까운 시일 안에 글리세롤 수요를 초과할 것으로 예상되고 있다. 본 연구에서는 글리세롤의 유효 이용 및 처리 측면에서 돈분과의 혼합 소화 가능성을 타진하였다. 글리세롤이 13.8 g/L 로 투입된 경우 돈분 단독 소화에 비해 메탄 생성량과 속도가 각각 90%, 120% 향상되어 혼합 기질로 사용될 수 있음을 보였으며, 글리세롤로부터 메탄의 수율은 232 mL/g였다. 그러나 27.5 g/L 이상의 농도에서는 저해작용으로 인해 메탄 생성 속도가 감소되었다. 돈분과의 혼합 소화 시 글리세롤의 최적 주입 농도는 13.8 g/L부근인 것으로 사료된다.

핵심 용어 : 혼합 소화, 글리세롤, 저해, 돈분

1. Introduction

Glycerol ($CH_2(OH)CH(OH)CH_2(OH)$) is the inevitable by-product from biodiesel process[5]. Biodiesel industry is rapidly expanded and is expected to increase exponentially in the near future[8]. Pure glycerol has more than 2,000 different applications[2]. However, the increased production of crude glycerol is expected to exceed the commercial demand for purified glycerol[4]. Furthermore, it is too costly to refine the crude glycerol to a high purity, especially for medium and small biodiesel producers[7]. Anaerobic digestion of crude glycerol would be a good option for the value-added use of crude glycerol from biodiesel [6]. Glycerol is basically degradable to volatile fatty acids and alcohols such as propionate, acetate, and 1,3-propandiol, which in turn are converted to methane in anaerobic condition. However, it may cause substrate inhibition or VFA accumulation to anaerobic microorganisms at certain level[1]. Although the inhibitory level of glycerol on anaerobic digestion is not reported yet, co-digestion with existing organic waste rather than digestion of sole crude glycerol would give higher biogas production. The main aim of this study is to evaluate the feasibility of crude glycerol as co-substrate of anaerobic digestion of swine manure.

2. Material and Methods

Crude glycerol was collected from a biodiesel plant. Swine manure and digester sludge were obtained from a swine farm and a digester treating swine manure from the farm, respectively. [Table 1] shows characteristics of the crude glycerol, the swine manure and the digester sludge. The crude glycerol and the swine manure were stored in a refrigerator at 4℃, while the digester sludge was kept at 35℃ until use.

Batch experiment was performed using 250 mL serum bottles (160 mL of working volume). The batch experiment was designed to simulate a digester fed with swine manure and crude glycerol. 12 bottles were for blanks (digester sludge and dilution water only), control (swine manure and digester sludge only), and four different crude glycerol content with their duplicates. The bottles were filled with digester sludge, swine manure, crude glycerol and dilution water as shown in

[Table 1] Characteristics of Crude Glycerol, Swine Manure and Digester Sludge

Parameter	Crude glycerol	Swine manure	Digester sludge
TS (g/L)	–	64.6	28.2
VS (g/L)	1.10E3[a]	47.5	15.1
COD (g/L)	1.43E3	43.8	13.8
VSS (g/L)	–	23.8	11.5
VFA (g/L as HAc)	–	3.3	0.6
Alkalinity(g/L as $CaCO_3$)	–	13.6	10.2

[a] Measured by density. Typical VS measurement was not suitable for crude glycerol owing to vaporization of methanol (b.p. 64.7℃) at 105℃.

[Table 2] Initial pH of the content in each bottle was adjusted to 7.1~7.2. Then, the bottles were purged with nitrogen gas, capped, and placed in a shaking incubator with 180 rpm at a 35℃. Biogas production and its constituents were measured periodically from each bottle to estimate methane production rate. Methane composition was measured using a GOW-MAC Series 350 gas chromatograph equipped with a thermal conductivity detector. The column was a 2.43m x 0.64 cm SS 350B Hayesep DB 80/100 and the operational temperatures of the injection port, oven and the detector were 150℃, 50℃, and 100℃, respectively. Helium was used as the carrier gas at a flowrate of 30 mL/min. Measured methane production was corrected to standard temperature (0℃) and pressure (760 mmHg) (STP).

3. Results and Discussion

The batch test was conducted during 49 days. [Fig. 1] shows cumulative methane production of the four crude glycerol-added conditions and the control (without glycerol) after normalization with their blanks. [Table 3] summarized the methane production parameters found in this study.

The highest methane production (1079 mL) and methane productivity (79 mL/g VS_{seed}/d) were found at 13.8 g crude glycerol/L (Gly 1). The methane

[Table 2] Experimental Design of Batch Test

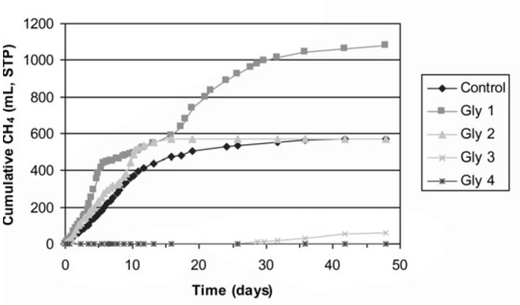
Parameter	Control	Gly 1	Gly 2	Gly 3	Gly 4	Blank
Digester sludge (mL)	100	100	100	100	100	100
Swine manure (mL)	40	40	40	40	40	0
Crude glycerol (mL)	0	2	4	8	16	0
Dilution water (mL)	20	18	16	12	4	60
Total substrate (g/L)[a]	11.9	25.7	39.4	66.9	121.9	0
F/M ($g_{substrate}$/g VS_{seed})	1.3	2.7	4.2	7.1	12.9	0
Crude glycerol/Swine (g/g VS)	0	1.2	2.3	4.6	9.3	–
Crude glycerol (g/L)	0	13.8	27.5	55.0	110.0	0
Glycerol (g/L)[b]	0	9.6	19.2	38.5	77.0	0
Methanol (g/L)[c]	0	4.2	8.3	16.5	33.0	0

[a] Sum of swine manure (based on VS value) and crude glycerol (based on density).

[b and c] Assumed from 70:30 ratio

yield and productivity were increased by 90% and 120%, respectively, compared to control (swine manure only). CH_4 yield of crude glycerol was estimated to be 232 mL/g (((CH_4 from Gly 1)−(CH_4 from control)) / (Glycerol in Gly 1) = (1079 mL−567 mL) / (2.2 g)). At 27.5 g crude glycerol/L (Gly 2), CH_4 productivity was still higher than control (58%), but CH_4 production did not increase substantially (1%). Moreover, at 55.0 and 110.0 g crude glycerol/L (Gly 3 and Gly 4), CH_4 production was lower than the control. It implied that too high crude glycerol concentration may inhibit microbial activity and growth in a digester.

Crude glycerol consists of glycerol and methanol. Although both compounds are regarded as easily-biodegradable, they may cause substrate inhibition or volatile fatty acids (VFA) accumulation. However, criteria for their maximum concentrations on methanogenic microflora have not been addressed. Cheng et al. (2005)[1] reported the effects of glycerol concentration on a pure culture producing 1, 3-propanediol. In the study, inhibition on productivity was found at glycerol concentration above 50 g/L. Fukuzaki and Nishio (1997)[3] operated a UASB reactor at different methanol concentration (0.5 to 8.6 g/L). Even at the highest methanol concentration, methanol removal efficiency showed higher than 85%. Therefore, we anticipated the best result would be found at Gly 2 (8.3 g methanol/L) or Gly 3 (38.5 g glycerol/L). However, the optimum condition in this study was lower than the expected. Unknown factors such as synergic interaction among glycerol, methanol and swine manure could cause the inferior methane production at Gly 2, Gly 3 and Gly 4.



[Fig. 1] Cumulative methane production (normalized with the blank).

4. Conclusion

At the concentration of 13.8 g/L, crude glycerol acted as a good supplemental feedstock material to swine manure digester. It enhanced methane production and productivity by 90% and 120%, respectively. Methane yield of crude glycerol at the condition was estimated to be 232 mL/g. However, at above 27.5 g/L, it showed inhibitory effect on methanogenic activity. Optimum concentration of crude glycerol would be near to 13.8 g/L.

[Table 3] Methane Production Parameters

Parameter	Control	Gly 1	Gly 2	Gly 3	Gly 4
CH_4 production (mL)	567	1079	570	58	0
CH_4 yield of crude glycerol (mL/g)[a]	−	232	1	−	−
Increased CH4 production compared to the control (%)	−	90	1	−	−
CH_4 productivity (mL/g V_{Sseed}/d)[b]	36	79	57	3	0
Increased CH_4 productivity compared to the control (%)	−	120	58	−	−

[a] Normalized with the CH_4 production in the control

[b] Estimated from the 5 consecutive data points in exponential growth

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